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## **A 'Building Block' Approach To Mixed-Colloid Systems Through Electrostatic Self-Organization**

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### **ABSTRACT**

We have developed a 'building block' approach to electrostatically-mediated construction of modular self-assembled colloid-colloid ensembles. Our strategy involves functionalization of one type of colloidal building block with a primary amine, and a counterpart building block with a carboxylic acid derivative (Scheme 1). By combining the two systems, acid-base chemistry followed by immediate charge-pairing resulted in the spontaneous formation of electrostatically-bound mixed-colloid constructs. The shape and size of these ensembles was controlled via variation of particle size for the two components and their stoichiometries.

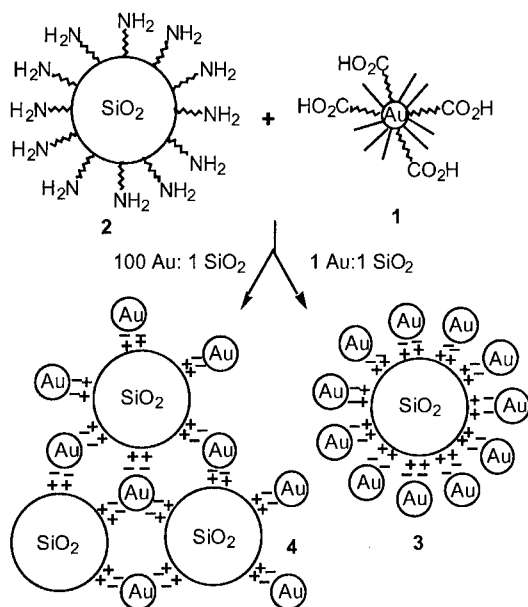
### **INTRODUCTION**

Molecular self-assembly is the association of molecules into structurally well-defined, stable aggregates via thermodynamically-controlled non-covalent interactions. Application of self-organization to multi-scale ordering of colloidal nanoparticles provides a platform for the creation of macroscopic devices. The ability to finely control the spatial arrangement of nanoscopic entities in composite arrays allows for the creation of materials with interesting electronic [1], optical [2], optoelectronic [3], and magnetic properties [4].

For these applications to be realized, however, preparation of physically and chemically diverse nanocomposite materials is a major goal. Recent examples of these materials include biomolecule-colloid [5], colloid-colloid [6], polymer-colloid [7], dendrimer-colloid [8], and sol gel-colloid materials [9]. We report here a 'building block' approach to the construction of modular colloid-colloid ensembles through electrostatically-mediated self-organization.

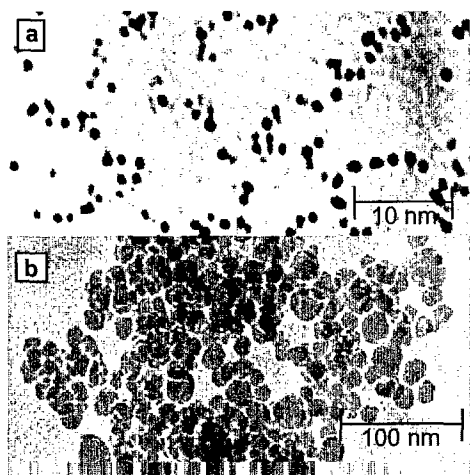
### **EXPERIMENTAL DETAILS**

Our methodology entailed functionalizing one type of colloidal building block with a primary amine, and a counterpart building block with a carboxylic acid derivative (Scheme 1). By combining the two systems, acid-base chemistry followed by immediate charge-pairing would result in the spontaneous formation of electrostatically-bound mixed-colloid constructs. These systems are easily discriminated both in size and properties, and can be synthesized in a straightforward manner.



**Scheme 1:** Illustration of carboxylic acid-functionalized gold colloid **1** reacting with amine-functionalized silica colloid **2**, providing differently derived morphologies **3** and **4**. For colloid **1**, the wavy lines represent the propyltrimethoxysilyl-tether. For **2**, wavy lines are associated with decanethiol ligands; the straight lines correspond to octanethiol ligands. 100:1 Au 1:SiO<sub>2</sub> **2** is equivalent to 100x1 mg/mL Au **1** colloid solution added to 1x1 mg/mL SiO<sub>2</sub> **2** colloid solution.

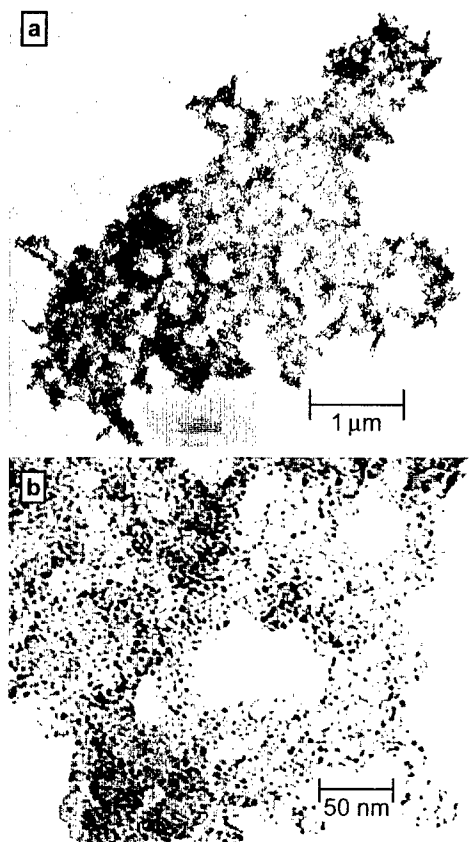
Carboxylic acid-functionalized gold particles **1** were prepared by ligand exchange of commercially available 11-mercaptoundecanoic acid with octanethiol-functionalized gold colloids [10]. These were then dispersed in a THF/MeOH (3/1) medium to 0.5% w/v. Amine-derived colloids **2** were prepared by reacting 15 nm silica particles with 3-aminopropyltrimethoxysilane [11], and subsequently dispersed in a THF/MeOH (3/1) medium to 0.5% w/v. TEM analyses of **1** and **2** were performed to verify the structure of these colloidal systems. The resulting pictures show that the Au colloids **1** (Figure 1b) were about 2 nm in diameter, while the silica colloids **2** (Figure 1a) were 15 nm in diameter.



**Figure 1:** TEM micrographs of (a) Au **1** and (b) SiO<sub>2</sub> **2** colloid systems.

## DISCUSSION

Initial studies focused on combining solutions **1** and **2** in a 1:1 ratio [12], where rapid aggregation of the gold colloid suspension was seen. The low magnification TEM (Figure 2a) shows the organized arrangement attained by this mixed-colloid system. The presence of giant ‘fractal-like’ superstructures ranging *ca.* 4-5 *micrometers* in size is clearly visible. Higher magnification TEM micrographs (Figure 2b) clearly shows that each silica particle is surrounded by a number of smaller Au nanoparticles. These Au colloids are themselves attached to additional silica colloids, affording giant mixed-colloid superstructures. Another interesting feature is the regular spacing of Au colloids on the surface of the silica particles, arising from the coulombic repulsions between charge-paired units. This observation is in line with other charged colloid systems where charged metallic nanoparticles are known to electrostatically repel each other and are typically well separated on substrate surfaces [13]. As a control study, we replaced **1** with an alkyl-functionalized derivative, removing any capacity to undergo acid-base chemistry. As expected no aggregation took place, indicating that the structural morphology observed in the **1.2** aggregates arises from electrostatic self-assembly.



**Figure 2:** TEM micrographs of 1:1 Au 1:SiO<sub>2</sub> 2 system. Micrograph A is low magnification picture showing the giant fractal-like superstructure obtained. Micrograph B is high magnification image clearly showing the self-association present in 1:1 Au 1:SiO<sub>2</sub> 2 system. Au colloids appear dark, while silica nanoparticles appear light.

It has been demonstrated that controlling the Au density on silica colloid surfaces can lead to regulation of optical resonance [14]. We predicted we could manipulate the Au 1 colloid density and thus structural morphology of the mixed-colloid superstructure by increasing Au 1 equivalents. After combining solutions 1 and 2 at 20:1 and 100:1 respectively, and performing TEM studies, two distinct mixed-colloid morphologies were afforded. For the 20:1 system, the mixed-colloid assemblies obtained were 100-250 nm across, greatly reduced in size as compared to the giant superstructures attained for the 1:1 system. (Figure 3a). Also discernible was the increased density of Au colloids on the surface of the SiO<sub>2</sub> particles. As in the 1:1 system, the Au colloids were evenly spaced but the inter-gold colloid distance had decreased. For the 100:1 mixed-colloid system, the smallest colloidal clusters of all three systems were attained (Figure 3b). These constructs

consisted of only a small number of silica particles per cluster, ranging from 50-100 nm in size. Also visible is the complete surface coverage provided by the close packing of the Au colloids on the SiO<sub>2</sub> surface, with virtually no distance between the Au nanoparticles.

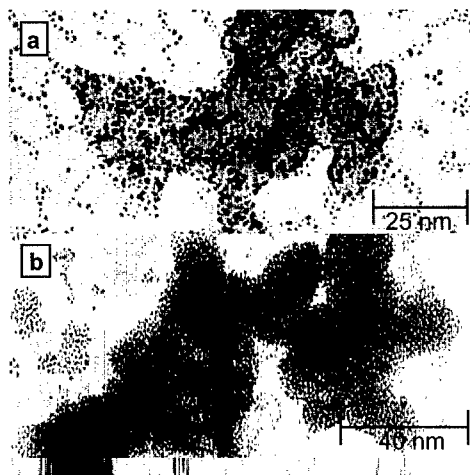


Figure 3: TEM micrographs of 20:1 and 100:1 Au 1:SiO<sub>2</sub> 2 mixed-colloid systems. Micrograph a corresponds to 20/1 system. Higher density of Au colloids, which remain evenly spaced, is seen. Micrograph b is associated with 100/1 system, and shows densely packed monolayer of Au 1 colloids electrostatically bound to the surface of 2.

## CONCLUSION

In summary, a facile methodology for constructing diverse mixed-colloid ensembles was established. It was demonstrated that the mixed-colloid architecture was controlled by both electrostatic-self assembly and concentration changes, regardless of the nature of the core.

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